

Surface Properties of GaN Fabricated by Laser Lift-Off and ICP Etching

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In this report, we describe the surface properties of a controlled thickness GaN microcavity which incorporates Zr_2O_3/SiO_2 DBR stacks for both the bottom and the top mirrors. The GaN microcavities were fabricated using laser lift-off and inductively coupled plasma etching. We also compared etch rates, surface composition, and surface roughness between grown GaN and GaN fabricated by laser lift-off and ICP etching.

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I. INTRODUCTION

Following the successful development of high-performance AlGaInN light emitting diodes (LEDs) and laser diodes, research attention is now being directed towards other III-N devices, including short-wavelength vertical cavity surface-emitting lasers (VCSELs). There have been some reports claiming that stimulated emission in vertical cavity like structures has been observed in GaN and InGaN layered structures under intense optical pumping [1-4]. The fabrication of a high performance DBR (distributed Bragg reflector) remains one of the major hurdles to overcome for the realization of viable III-nitride VCSELs. The obvious obstacle concerning the realization of nitride VCSEL structures with dielectric DBRs is the formation of high quality bottom DBRs.

Laser lift-off (LLO) of III-nitrides from sapphire substrates is a promising method for electronic device integration and GaN substate creation. Laser lift-off has recently been demonstrated for fabrication of a free-standing InGaN multiple quantum well LED without any degradation to the LED devices due to the laser-separation process [5, 6]. The fabrication of optically pumped VCSELs [7], vertical-structure blue LEDs [8], and large-area free-standing GaN substrates [9] have been also demonstrated using LLO.

Dry etching is essential for the fabrication of AlGaInN VCSELs, as it is for other optoelectronic devices, due to the practical inapplicability of wet-chemical etching to

nitride alloys [10,11]. High density plasma etching and chemically assisted ion beam etching (CAIBE) have been considered as the most suitable methods for patterning III-nitrides. For the fabrication of a vertical microcavity using LLO, the removed GaN was then etched-back in order to remove the uppermost low quality GaN nucleation layer, control the microcavity length and clean the surface of the GaN. The etched GaN surface must be smooth without any etch-induced damages during the etch-back until the etch endpoint. In other works, ECR plasma etching and CAIBE were used to reduce the thickness of the optical structure, improve the surface roughness, and form a mesa structure [3,5,8]. However, detailed etch condition or surface property investigations have not been fully reported even though effects of plasma etching conditions on the surface properties and the optical properties of fabricated devices may be important before final mirror depositions or contact formation. In this work, we investigated the surface properties of controlled-thickness GaN microcavities fabricated by plasma etching and laser lift-off.

II. EXPERIMENTS

A multilayer of 10.5 pairs of SiO_2/ZrO_2 was first deposited on a 2 μ m-thick GaN thin film which had been grown on sapphire by using metalorganic chemical vapor deposition (MOCVD), by E-beam evaporation. The pre-processed DBRs on GaN structure was then bonded onto the surface of a p-type Si (001) wafer using an epoxy [7, 8], forming a sapphire/GaN/DBRs/Si substrate. Laser lift-off and transfer of the GaN with bottom DBRs from

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sapphire was accomplished using a single 600-mJ/cm² pulse with a wavelength of 248 nm from a KrF laser directed through the transparent sapphire substrate with its backside-polished. Following the laser irradiation, a low-temperature annealing at 40 °C completed the separation process by melting the Ga-rich interface. By this two-step process, films up to 1 cm² in area were transferred by a 0.03 cm² beam spot across the entire sample.

The GaN attached on the Si substrate was then etched-back using inductively coupled plasmas and a dilute HCl solution in order to remove the uppermost low-quality GaN nucleation layer, control the microcavity length, and clean the surface of the GaN. The etching was performed as a function of composition of Cl₂/BCl₃ in Cl₂/BCl₃/Ar mixtures with a constant flow rate of 20 % Ar while other conditions were fixed at an inductive power of 600 W, a bias power of 150 Watts, a pressure of 10mTorr, a total gas flow rate of 50 sccm, and a substrate temperature of 20 °C. These etch conditions were optimized from previous etch works on GaN and AlGaIn [12]. To compare the etch rates of GaN before and after LLO work, we used some pieces of GaN with patterned photoresists without the first DBR mirror deposition during etching. Prior to final mirror deposition, the GaN was cleaned in acetone, then in ethanol, and then rinsed in DI water. Next, the GaN was placed in a 1: 2 HCl mixture of HCl : DI water for 2 min, followed again by a through DI water rinse. Finally, a GaN microcavity was produced by the deposition of a second dielectric mirror.

The etch rates were calculated from the depth of etched features measured with a Detak stylus profilometer after the photoresist was removed. The surface morphologies and cross-sectional views were observed using scanning electron microscopy (SEM), and the root-mean-square (rms) surface roughness was quantified using an atomic force microscope (AFM, Digital Instruments Dimension 3000) operating in the tapping mode with a Si tip. Surface compositions were measured by using X-ray photoelectron spectroscopy (XPS, Fison's System ESCALAB 200i) with a monochromatic Mg α source (1253.6 eV energy). The Ga 3d, N 1s, Al 2p, O 1s, and C 1s core level peaks were chosen for study, and Cu 2p at 932.65 eV and Au 4f at 83.86 eV were taken as the energy references. The data were taken at take-off angles of 15°, 30°, 45°, 60°, 75° and 90° from the surface to enhance surface sensitivity.

III. RESULTS AND DISCUSSION

Before bonding to a Si substrate, a multilayer of 10.5 pairs of SiO₂/ZrO₂ was first deposited on GaN. The measured reflectivity of the SiO₂/ZrO₂ DBR was centered near 420 nm with a peak reflectivity of 99.5 % and the high-reflectivity bandwidth in excess of 80 nm [5]. We had bonded the surface of this mirror to a Si substrate, the sapphire was removed by laser, followed by heating.

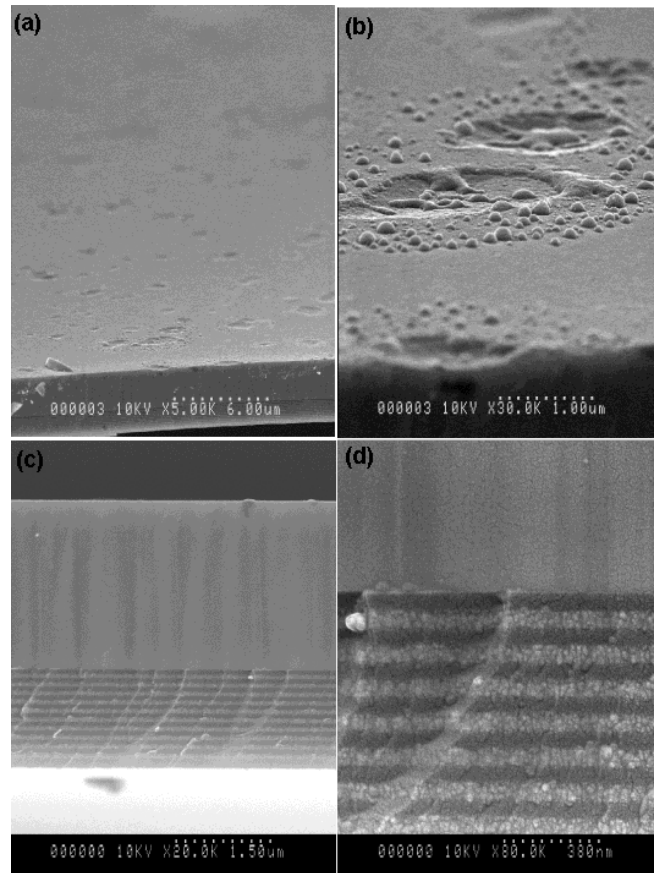


Fig. 1. SEM images of GaN fabricated by laser lift-off (LLO).

Figure 1 show SEM images of the removed GaN with bottom DBRs fabricated by LLO. Good adhesion between the DBRs and GaN is observed. However, the removed GaN surface, as shown in this figures, has damaged areas, including with residual droplets of byproducts from the LLO process. Even though no degradation of either the physical properties or the device performance of the GaN or the LED structure fabricated by LLO in previous works [7, 8, 13, 14], inhomogeneous surfaces with damaged areas were observed in our work. The roughness was especially increased by pits. Figure 1(b) shows enlarged view of the pits, which are believed to have been formed by N₂ explosion, and droplets around them. The droplets, therefore, are believed to be mainly composed of Ga and Ga-oxide. In addition to the damaged layer, since the separation occurs at the interface of the original GaN on sapphire, which is a highly defective region due to GaN buffer layer being grown at the low temperature, it is desirable to remove the damaged layer from the separated surface by using a proper method.

The root-mean-square (rms) value of the surface roughness over the entire atomic force microscopic field of view of 400 μm² was approximately 32±5 nm. The backside roughness of the polished sapphire before LLO work and the beam uniformity of laser source may af-

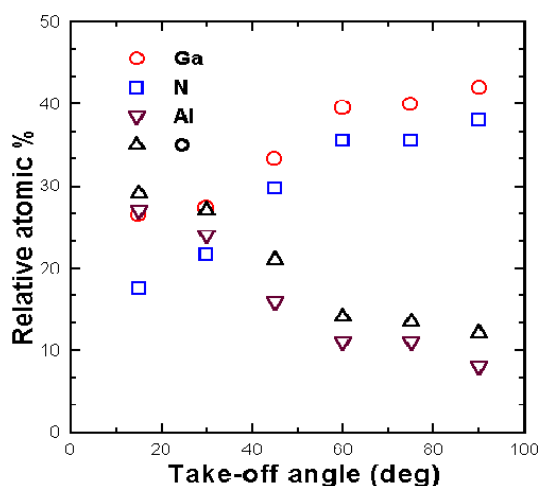


Fig. 2. Surface composition of LLO GaN as a function of take-off angle measured by X-ray photoelectron spectroscopy (XPS).

fect the damaged areas. The surface composition near the removed GaN was measured by angle resolved XPS analysis, and the removed GaN was made up of Al and O, as well as Ga and N. Figure 2 summarizes the relative atomic percents of Ga, N, Al, and O as functions of the take-off angle. These results clearly show that Al and O were found near the surface and these compositions were distributed in depth. The ratio of Ga/N measured by XPS was 2.5 at a take-off angle of 15, and this value decreased to 1.1 with increasing take-off angle. In particular, the steep increase in the Al and the O atomic percents at lower take-off angles indicated that the N composition was depleted on the topmost natural oxide layer, resulting in the formation of a highly nonstoichiometric surface where Ga-oxide and Al-oxide were dominant. These surface composition data, including those for Al and O, were also confirmed by other reports, which indicate that the changes in the structural quality and the presence of interdiffusion between components, such as Al and O, are confined to approximately the first 50 nm of the epilayer thickness [13].

On the GaN/DBR removed by LLO, the top DBRs are followed to sandwiched vertical GaN microcavity by two DBRs. For a good GaN microcavity, surface contamination and roughness must be reduced by post-treatments. The ICP etching was performed to remove the uppermost low quality GaN nucleation layer, control the microcavity length, and clean the surface of the GaN. $\text{Cl}_2/\text{BCl}_3/\text{Ar}$ plasmas were used in this work to obtain a controllable etch rate of the Al containing GaN surface, to reduce the surface roughness, and to remove damaged areas on the removed GaN. That is, an optimal addition of BCl_3 gas to Cl_2 was very effective for etching Al component such as AlO_x effectively. The addition of Ar also improved surface morphologies [10, 12, 15–17]. We etched GaN samples fabricated by LLO (LLO GaN) for various amounts of Cl_2/BCl_3 in the $\text{Cl}_2/\text{BCl}_3/\text{Ar}$ mixture

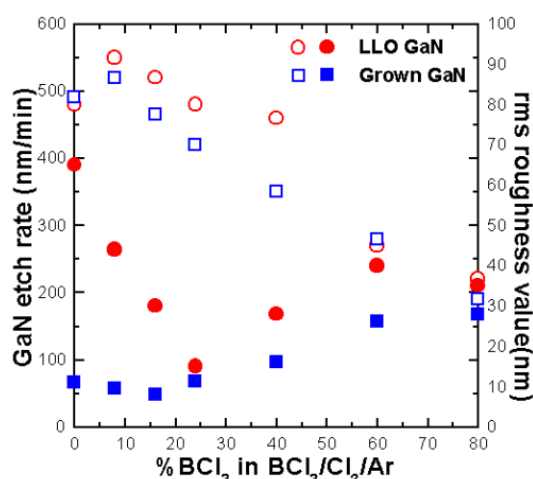


Fig. 3. Etch rate (open symbols) and surface roughness (solid symbols) of as-grown GaN and LLO GaN as functions of the BCl_3 composition in $\text{Cl}_2/\text{BCl}_3/\text{Ar}$ plasmas.

with a constant flow rate of 20 % Ar. The same experiment was also performed with GaN grown on sapphire (Grown GaN) for a comparison. The etch rates of the two types of GaN samples and rms roughness values are shown in Fig. 3. For the LLO GaN samples, the GaN etch rate increased with increasing BCl_3 percent, and the maximum etch rate was obtained with an 8 % BCl_3 gas mixture. Also, until 40 % of BCl_3 had been added to Cl_2 , the GaN etch rates were higher than those for an 80 % $\text{Cl}_2/20$ % Ar plasma. For the grown GaN samples, the maximum etch rate was obtained at the same gas mixture of 8 % BCl_3 . However, the GaN etch rates were lower than those for an 80 % $\text{Cl}_2/20$ % Ar plasma after the BCl_3 percentage had been increased above 16 %. In the both GaN samples, the maximum etch rate was about 550 nm/min for LLO GaN samples and 520 nm/min for grown GaN with a 72 % $\text{Cl}_2/8$ % $\text{BCl}_3/20$ % Ar plasma and further increases in the BCl_3 flow rate decreased the etch rate. The differences in the etch rates between the two samples were ascribed to the material quality and surface composition, which included Al and O. We found that lower quality GaN fabricated by LLO had higher etch rates than the grown GaN.

The surface morphologies were evaluated using AFM, and the rms values for non-etched GaN fabricated by LLO and GaN grown on sapphire were 32 ± 5 nm and 5 ± 0.6 nm, respectively. The surface roughness of the as-grown GaN sample was increased after ICP etching regardless of the gas mixture composition. However, the smoothest surface was obtained from the sample etched by a 16 % BCl_3 mixture and the roughness increased with BCl_3 content. In the case of the laser lift-off sample, ICP etching with a 24 % BCl_3 mixture left the smoothest surface (rms value of ~ 15 nm) while decreasing the BCl_3 content dramatically increased the roughness. These rough surfaces of etched GaN, even after etching with higher etch rate compared to that of grown

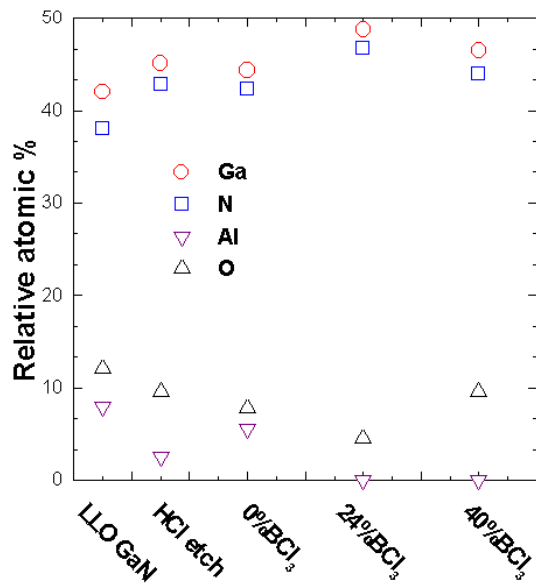


Fig. 4. Surface analysis data of LLO GaN after various post-treatments. The XPS data were taken at a 90° take-off angle. HCl etching was used in this work after ICP etching.

GaN, were ascribed to the surface composition of Al-containing damaged layers (etched under 24 % of BCl_3) and insufficient etch depth to remove damaged layer due to lower etch rates (etched over 40 % of BCl_3). Even though the absolute rms value may be changed with the GaN surface status defined by pre-processing, an optimized gas combination can give a smooth surface for final device fabrication.

We also observed surface composition by XPS measurement after ICP etching, and we used dilute HCl wet etching to remove Ga or Ga-oxide and Al, together. Five types of samples were used and the take-off angle of 90° was taken in the XPS analysis. For the first sample, GaN removed prior to post-treatments. The second set was prepared by dipping the GaN in the dilute HCl solution described in section II. The other three samples were etched using an 80 % Cl_2 /20 % Ar plasma, a 56 % Cl_2 /24 % BCl_3 /20 % Ar plasma, and a 40 % Cl_2 /40 % BCl_3 /20 % Ar plasma, respectively. These three samples were dipped in a dilute HCl solution after ICP etching. Figure 4 shows the effects of various post-treatments on the surface composition formed by LLO. The relative atomic percentage of the GaN surface was determined by using an areal integration of the XPS intensity in each composition's narrow scan data. As shown in the figure, the use of HCl dipping followed by plasma etching as a post-treatment led to a decrease in the amount of Al and O near GaN and a decrease in the Ga/N ratio from 1.1 to 1.05. For comparison, grown GaN was composed of Ga : N : O = 47.4 : 45.2 : 7.4. The O composition related to the oxide, such as Ga-oxide or Al-oxide, could be reduced until about 5 % for 64 % Cl_2 /16 % BCl_3 /20 % Ar followed by HCl dipping even though all of GaN used in

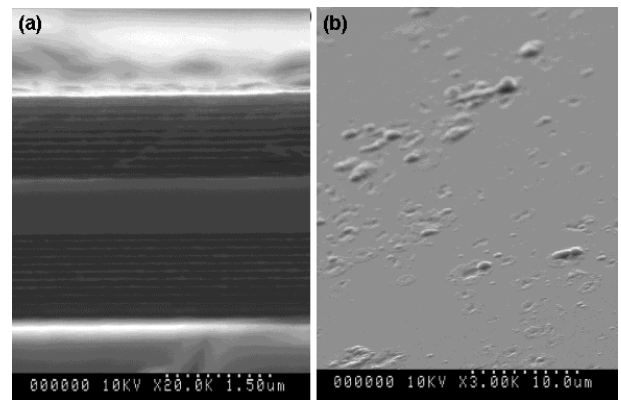


Fig. 5. SEM images of a GaN microcavity fabricated by using laser lift-off and ICP etching before deposition of the top mirrors.

the XPS analysis contained O due to air contamination. The Al composition could be fully removed on the GaN treated with a 56 % Cl_2 /24 % BCl_3 /20 % Ar plasma or a 40 % Cl_2 /40 % BCl_3 /20 % Ar plasma while the Al composition still remained after only HCl dipping or 80 % Cl_2 /20 % Ar plasma treatment followed by HCl dipping. The addition of BCl_3 (almost 24 % BCl_3) to the Cl_2 /Ar plasma etching was more effective in reducing Al and O near the GaN surface, but O increased with an addition of over 40 % of BCl_3 to the Cl_2 /Ar plasma due to B_xO_y formation on the etched GaN surface. As a result, we found a combination of dilute HCl wet etching and ICP etching with BCl_3 gas to be very effective in reduction of surface damage. The thickness of the GaN cavity (that is, the microcavity length) could be controlled by varying the GaN etch depth, which is varied with ICP etch conditions.

Figure 5 show SEM images of GaN sandwiched by two DBRs; the structure consists of a GaN layer sandwiched by two dielectric mirrors. The fabrication involved removing the sapphire substrate by laser-lift off and etching the GaN layer before deposition of the top DBR, thereby reducing the GaN thickness from its initial value of $\sim 2 \mu\text{m}$ to $0.7 \mu\text{m}$. GaN was etched using the 64 % Cl_2 /16 % BCl_3 /20 % Ar plasma described previously, and the top DBR was deposited after HCl dipping. The surface of the GaN cavities was similar to that of previous step before the top DBRs and the ICP etching could reduce the damaged area. The surface of the GaN microcavity fabricated using post-treatments, including plasma etching, was very smoother than that of the GaN microcavity fabricated with post-treatments.

The spectroscopic characterization of the microcavities shown in Fig. 5 is reported in detail elsewhere [18]. In brief, the $\text{SiO}_2/\text{ZrO}_2$ DBRs used in this study were designed to have a high-reflectivity band centred at 420 nm with a bandwidth in excess of 80 nm. The characteristics of the DBRs allowed the observation of several cavity modes between ~ 370 and 470 nm in the reflectance

and the low-temperature PL spectra obtained from the microcavity samples. Simulations of the mode positions were in good agreement with the expected GaN layer thicknesses. Finesse values were calculated from widths of spectrally filtered PL peaks. A finesse of ~ 10 was obtained for both the etched and non-etched GaN cavities, demonstrating that the ICP etch process caused no degradation in the optical properties. If equal reflectivities are assumed at both GaN/DBR interfaces, these finesse value corresponds to a reflectivity of $\sim 85\%$. Subsequently, we obtained a higher finesse of ~ 50 for microcavity fabricated using similar LLO and ICP processing, but incorporating InGaN QWs [19]. This value is similar to the best values reported by other groups [3].

IV. SUMMARY

A GaN surface, separated from a sapphire substrate by using LLO process, has damaged areas containing residual droplets of material produced by the LLO process. The damaged parts of GaN could be reduced by optimized HCl dipping and ICP etching before top DBR deposition. For the ICP etching, a BCl_3 -containing plasma was very important in removing damaged layers, including those with gallium oxide or Al. The surface morphology measured by using AFM also decreased to an rms value of 15 nm from a value of 32 nm after etching. The thickness of the GaN cavity could be controlled by varying the GaN etch depth, which was controllable via the ICP etch conditions.

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REFERENCES

- [1] T. Someya, K. Tachibana, J. Lee, T. Kamiya and Y. Arakawa, *Jpn. J. Appl. Phys.* **37**, L1424 (1998).
- [2] I. L. Kerstnikov, W. V. Lundin, A. V. Sakharov, V. A. Semenov, A. S. Usikov, A. F. Tsatsul'nikov, *Zh. I. Alferov*, N. N. Ledentsov, A. Hoffman and D. Bimberg, *Appl. Phys. Lett.* **75**, 1192 (1999).
- [3] Y. K. Song, H. Zhou, M. Diagne, A. V. Nurmikko, R. P. Schneider, C. P. Kuo, M. R. Krames, R. S. Kern, C. Coman and F. A. Kish, *Appl. Phys. Lett.* **76**, 1662 (2000).
- [4] J. M. Redwing, D. A. S. Loeber, N. Anderson, M. A. Tischler and S. Flynn, *Appl. Phys. Lett.* **69**, 1 (1996).
- [5] W. S. Wong and T. Sands, *Appl. Phys. Lett.* **77**, 2822 (2000).
- [6] W. S. Wong, T. Sands, N. W. Cheung, M. Kneissi, D. P. Bour, P. Mei, L. T. Romano and N. M. Johnson, *Appl. Phys. Lett.* **75**, 1360 (1999).
- [7] R. W. Martin, T. Kim, D. Burns, I. M. Watson, M. D. Dawson, T. F. Kraus, J. H. Marsh, R. M. De. La. Rue, S. Romani and H. Kheyrandish, *Phys. Stat. Sol.(a)* **176**, 67 (1999).
- [8] Y. K. Song, M. Diagne, H. Zhou, A. V. Nurmikko, R. P. Schneider and T. Takeuchi, *Appl. Phys. Lett.* **77**, 1744 (2000).
- [9] M. K. Kelly, R. P. Vaudo, V. Phanse, L. Gorgens, O. Ambacher and M. Stutzmann, *Jpn. J. Appl. Phys.* **38**, L217 (1999).
- [10] S. J. Pearton, J. C. Zolper, R. J. Shul and F. Ren, *J. Appl. Phys.* **86**, 1 (1999).
- [11] H. S. Kim, G. Y. Yeom, J. W. Lee and T. I. Kim, *Thin Solid Films* **341**, 181 (1999).
- [12] H. S. Kim, T. Kim, K. S. Kim, I. M. Watson, R.W. Martin, J. H. Marsh, R. M. De Ra Rue and M. D. Dawson, in *Proceeding of Int. Workshop on Nitride Semiconductors, IPAP Conf. Series 1*, 750 (2001).
- [13] E. A. Stach, M. Kelsch, E. C. Nelson, W. S. Wong, T. Sands and N. W. Cheung, *Appl. Phys. Lett.* **77**, 1819 (2000).
- [14] W. S. Wong, Y. Cho, E. R. Weber, T. Sands, K. M. Yu, J. Kruger, A. B. Wengrow and N. W. Cheung, *Appl. Phys. Lett.* **75**, 1887 (1999).
- [15] H. S. Kim, D. H. Lee, G. Y. Yeom, J. W. Lee and T. I. Kim, *Vacuum* **56**, 45 (2000).
- [16] Y. H. Lee, H. S. Kim, G. Y. Yeom, J. W. Lee, M. C. You and T. I. Kim, *J. Vac. Sci. Technol. A* **16**, 1478 (1998).
- [17] H. S. Kim, J. W. Lee, T. I. Kim and G. Y. Yeom, *J. Vac. Sci. Technol. A* **17**, 2214 (1999).
- [18] R. W. Martin, P. R. Edwards, H. S. Kim, K. S. Kim, T. Kim, I. M. Watson, M. D. Dawson, Y. Cho, T. Sands and N. W. Cheung, *Appl. Phys. Lett.* **79**, 3029 (2001).
- [19] P. R. Edwards, R. W. Martin, H. S. Kim, K. S. Kim, Y. Cho, I. M. Watson, Y. Cho, T. Sands, N. W. Cheung and M. D. Dawson, *Phys. Stat. Sol.(b)* **228**, 91 (2001).